

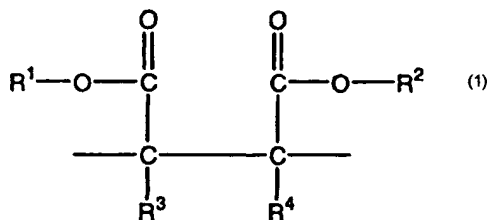
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(54) Title: LEVELLING AGENT AND ANTI-CRATERING AGENT



20,0 ≤ m ≤ 4 and 0 ≤ p ≤ 20, wherein X is a spacer moiety selected from the group consisting of esters, amides, sulfoamides, mercapto groups, polyurethane groups and alkyl groups, wherein R²_i is H, a metal moiety, an (alkyl)ammonium moiety or an alkyl group, C_in?F_i2n+1?-(CH_i2?)_im?-, AC_in?F_i2n?-(CH_i2?)_im?-, C_in?F_i2n+1?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?-, AC_in?F_i2n?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?-, AC_in?F_i2n?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?'-X or C_in?F_i2n+1?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?'-X; wherein A = H, Cl, Br, I, C_i1-12? alkyl or OC_i1-12? alkyl, wherein 4 ≤ n ≤ 20, 0 ≤ m ≤ 4 and 0 ≤ p ≤ 20, wherein X is a spacer moiety selected from the group consisting of esters, amides, sulfoamides, mercapto groups, polyurethane groups and alkyl groups, wherein R³_i and R⁴_i are independently selected from the group consisting of H, alkyl-groups and phenyl-groups and wherein R⁵_i is H and/or methyl group..

(57) Abstract: Use of a polymer as a levelling agent or anti-cratering agent, said polymer comprising at least one fluorinated unit represented by formula 1, (Formula 1) wherein R²_i is a moiety represented by C_in?F_i2n+1?-(CH_i2?)_im?-, AC_in?F_i2n?-(CH_i2?)_im?-, C_in?F_i2n+1?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?-, AC_in?F_i2n?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?-, C_in?F_i2n+1?-(CH_i2?)_im?'-X, AC_in?F_i2n?-(CH_i2?)_im?'-X-AC_in?F_i2n?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?'-X or C_in?F_i2n+1?-(CH_i2?)_im?-(OCH_i2?CHR?5_i)_ip?'-X; wherein A = H, Cl, Br, I, a C_i1-12? alkyl or a OC_i1-12? alkyl, wherein 4 ≤ n ≤

Levelling agent and anti-cratering agent

The invention relates to the use of a polymer comprising a fluoroester as a levelling agent or anti-cratering agent. The invention further relates to particular polymers, which contain fluoro-ester moieties.

Difficulties related to the application of liquid resin solutions (liquid systems) such as paint, printing ink, plastic compounds and the like, to solid substrates are generally known in the art, in particular when the surface tension of the liquid system is high, and the surface tension of the solid substrate is lower.

Such liquid systems are typically composed of solvents, resins, and optionally pigments, extenders and additives. In particular, modern synthetic resins have a higher intrinsic surface tension by design and function, in comparison to traditional resins based on natural fatty acids and oils. Thus it may be more difficult to apply modern liquid systems such as modern 2-component systems like epoxies, polyester/melamines or polyurethanes, than to apply (conventional) alkyds.

If water is employed as a solvent, the surface tension of the liquid formulation is high by definition. This obligates the technician to use levelling and anti-crater agents to obtain an esthetic surface, which ensures its protective function through an uniform film. By reduction of the surface tension of the liquid system to a value below the surface tension of the substrate, spreading of the liquid is improved and the surface may level out to obtain an esthetically more attractive film. Craters are caused by contaminates, which enter the liquid film from the outside, or are already present on the substrate. In order to avoid cratering, the liquid systems need to have a lower surface tension than the contaminate itself, usually silicone or mineral oil droplets.

For the purpose of levelling, substrate wetting and anti-cratering, the market offers a variety of products, ranging from organically modified polysiloxanes to fluorocarbons, waxes and other anionic, cationic or electroneutral organic surfactants, which however show well-known disadvantages such as foam formation, foam stabilisation, surface slip, overcoatability problems, and incompatibility in the liquid systems, causing craters, haze, loss of gloss, migration, sweating and poor storage stability.

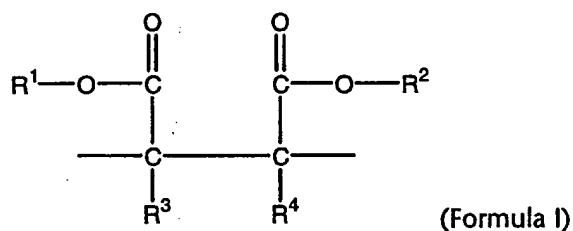
It has unexpectedly been found that by providing a polymer with an amount of fluorocarbons, the levelling and anti-cratering behaviour of a liquid resin systems can be achieved, without leading to overcoatability problems.

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The use of a number of fluorinated polymers as dirt and stain repellents is known from US 4,075,237 and US 5,770,656. The polymers described herein are applied to a finished substrate. When applied as such, such polymers usually lead to formation of craters and problems of overcoatability, due to their hydrophobicity, extremely low surface tension and their high content of fluorocarbons, which is the basis of their performance as a dirt and stain repellent.

It has now been found that particular polymers comprising an effective amount of certain ester moieties of unsaturated dicarboxylic-acids with certain fluorinated units are very suitable anti-cratering and/or levelling agents.

Accordingly, the present invention relates to the use of a polymer as a levelling agent or anti-cratering agent, said polymer comprising one or more fluorinated units represented by formula I,



wherein R^1 is a moiety represented by $C_nF_{2n+1}-(CH_2)_m-$,

$AC_nF_{2n}-(CH_2)_m-$, $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p-$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p-$, $C_nF_{2n+1}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p-X$ or $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p-X$;

wherein $A = H, Cl, Br, I$, a C_{1-12} alkyl or a $-OC_{1-12}$ alkyl,

wherein $4 \leq n \leq 20$, $0 \leq m \leq 4$ and $0 \leq p \leq 20$,

wherein X is a spacer moiety selected from the group consisting of esters, amides, sulfoamides, mercapto groups, polyurethane groups and alkyl groups,

wherein R^2 is H , a metal moiety, an (alkyl)ammonium moiety or an alkyl group,

$C_nF_{2n+1}-(CH_2)_m-$,

$AC_nF_{2n}-(CH_2)_m-$, $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p-$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p-$, $C_nF_{2n+1}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p-X$ or $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p-X$;

wherein A is H, Cl, Br, I , C_{1-12} alkyl or $-OC_{1-12}$ alkyl,

wherein $4 \leq n \leq 20$, $0 \leq m \leq 4$ and $0 \leq p \leq 20$,

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wherein X is a spacer moiety selected from the group consisting of esters, amides, sulphoamides, mercapto groups, polyurethane groups and alkyl groups, wherein R³ and R⁴ are independently chosen from the group consisting of H, alkyl-groups and phenyl-groups and wherein each R⁵ may be a H or a methyl group.

The use of a polymer according to the invention gives benefits such as complete wetting of the substrate. It may also help to prevent the formation of craters and pin-holes, to provide a smooth and/or equal levelling of the paint film without orange peel leading to improved esthetics of the dry film. Also, edge crawling, air-draft sensitivity, fish eyes and/or other dewetting effects of the liquid resin solution during the drying stage may be avoided or at least reduced significantly. Also, Bénard cells may be hidden and telegraphing may be avoided or reduced. Bénard cells are caused by turbulent movements of pigments in paint and the like during drying. Telegraphing is caused by areas of different surface tension in the substrate, which is transmitted to the top surface of the paint film. By adding a levelling agent in accordance with the invention, the surface may be straightened.

Additionally, it has been found that such a polymer exhibits low foam properties, which extend its use in comparison to conventional surfactants like polysiloxanes, ionic and electroneutral organic compounds, fluorocarbons and the like, to be used as defoaming agents. All this may be achieved without losing overcoatability of the dry film.

In a preferred embodiment the one or more fluorinated units of the polymer are represented by formula I wherein n is 4 - 14, more preferably 6 - 10.

Very good results have been achieved when using a polymer wherein at least 50%, preferably 70 - 100% of the fluorinated units of the polymer are represented by formula I wherein n is 4 - 10, preferably 6 - 10, and particularly wherein n is 6 or 8.

In another preferred embodiment the number of CH₂ units (m) in R¹ and optionally in R² is 1, 2, or 3. More preferably m in R¹ and/or R² is 2.

In another preferred embodiment the number of -(OCH₂CHR⁵) units (p) in R¹ and optionally in R² is 0, 6, 7 or 8.

In a preferred embodiment of the invention at least 50%, preferably 90 - 100% of the fluorinated monomeric units are mono-esters. An advantage of using a polymer with a high level of monoesters, is related to the ease of manufacturing such esters. Another

advantage of such a polymer is the fact that it can be rendered water-soluble in an efficient way through neutralisation of the remaining CO_2H -groups.

Very good results have also been achieved with a polymer wherein at least the majority of the R^1 moieties and optionally at least the majority of the R^2 represent a linear fluoroalkyl moiety.

Examples of particularly preferred fluorinated units (R^1, R^2) are (1H,1H,2H,2H)-pentadecafluorooctyl, (1H,1H,2H,2H)-heptadecafluorodecyl, (1H,1H,9H)-hexadecafluorononyl, (1H,1H,7H)-dodecafluoroheptyl, *N*-butyl and *N*-ethyl perfluorooctane sulphonamido ethyl, (1H,1H,2H,2H)-pentadecafluorooctyl heptaethoxylate and (1H,1H,2H,2H)-heptadecafluorodecyl heptaethoxylate.

Preferred examples of spacers (X) in R^1 and/or R^2 include esters, e.g. $-\text{O}-\text{CO}(\text{CH}_2)_x-$ or $-\text{CO}-\text{O}(\text{CH}_2)_x-$, amides, e.g. $-\text{NRCO}(\text{CH}_2)_x-$ or $-\text{CONR}(\text{CH}_2)_x-$, sulphonamides, e.g. $-\text{SO}_2\text{NR}(\text{CH}_2)_x-$, mercapto groups, e.g. $-\text{S}(\text{CH}_2)_x-$, polyurethane, e.g. $-\text{O}-\text{CONH}(\text{CH}_2)_x-$ or $-\text{NH}-\text{CO}_2(\text{CH}_2)_x-$, ethers, e.g. $-\text{O}(\text{CRHCH}_2)_x-$, linear or branched alkyl, e.g. $-(\text{CRH})_x-$ or alkenyl, e.g. $-\text{CR}=\text{CR}(\text{CRH})_x-$, wherein $x = 0 - 12$ and $\text{R} = \text{H}$ or C_{1-12} alkyl.

It has been found that the present invention offers very good anti-cratering features and/or may very well be used as a levelling agent in a variety of applications, e.g. in coatings and inks such as aqueous systems (e.g. emulsion laquers, such as lacquers based upon polyurethane, alkyds, acrylics, polyester-melamine), water-reducible systems (2K-polyurethane, alkyd, acrylic, epoxy, vinyl copolymers), (organic) solvent based systems (e.g. polyurethane-based, stoving alkyd/melamine- or polyester/melamine-based, epoxy-based, air-drying alkyds, nitrocellulose, CAB, unsaturated polyesters, acrylics, silicone resins, UV/EB-curing resins, vinyl copolymers, chlorinated rubber) and plastic compounds (hot and ambient curing unsaturated polyesters, epoxy, polyurethanes, polyvinylchloride).

A polymer used in accordance with the invention may be a co-polymer of different fluorinated units as defined by formula I. However, the polymer may also comprise other monomeric units (also referred to as co-monomers).

Examples of suitable comonomers are alkyl vinyl ethers, such as methyl vinyl ether, isopropyl vinyl ether, isobutyl vinyl ether, vinyl 2-methoxy ethyl ether, *n*-propyl vinyl ether, *t*-butyl vinyl ether, isoamyl vinyl ether, *n*-hexyl vinyl ether, 2-ethylbutyl vinyl ether, diisopropylmethyl vinyl ether, 1-methyl-heptyl vinyl ether, *n*-decyl vinyl ether, *n*-tetradecyl vinyl ether, and *n*-octadecyl vinyl ether.

Also, vinyl ethers of the following amino alcohols: ethanolamine vinyl ether, 2-dimethylamino ethanol vinyl ether, N-hydroxyethyl-m-toluidine vinyl ether, hydroxyethyl butyl aniline vinyl ether, and .beta.-piperidinoethanol vinyl ether, and the like.

Also useful are gamma substituted ethers, such as .alpha.-methylvinyl methyl ether, .alpha.-methylvinyl ethyl ether, .alpha.-amylvinyl methyl ether, and .alpha.-phenylvinyl ethyl ether; alicyclic and aralkyl vinyl ethers such as cyclohexanol vinyl ether, menthol vinyl ether, carvacrol vinyl ether, benzyl alcohol vinyl ether, .beta.-phenylethanol vinyl ether, tetrahydronaphthol vinyl ether, .beta.-decahydronaphthol vinyl ether, methylphenyl carbinol vinyl ether, butyl-cyclohexanol vinyl ether, and dihydroabictinol vinyl ether.

Additionally, vinyl aryl ethers such as vinyl phenyl ether, .alpha.-bromovinyl phenyl ether, .alpha.-phenylvinyl phenyl ether, vinyl m-cresyl ether, .alpha.-methyl vinyl p-cresyl ether, vinyl p-chlorophenyl ether, vinyl 2,4,6-trichlorophenyl ether, and vinyl .alpha.-naphthyl ether.

Useful copolymers of the polymers may be formed with vinyl esters, e.g. vinyl acetate, vinyl esters of substituted acids, such as for example, vinyl methoxyacetate, vinyl trimethylacetate, vinyl isobutyrate, isopropenyl butyrate, vinyl lactate, vinylcaprylate, vinyl pelargonate, vinyl myristate, vinyl oleate and vinyl linoleate; vinyl esters of aromatic acids, such as vinyl benzoate, vinyl alkoxybenzoates, vinyl octylphthalate, vinyl tetrachlorobenzoate, vinyl .beta.-phenyl butyrate, vinyl .beta.-naphthoate, and vinyl ethyl phthalate; vinylformate and vinylcarbonate derivatives such as vinylformate, vinylchloroformate, methylvinylchloroformate, vinyl methyl carbonate, vinyl ethyl carbonate, vinylphenylcarbonate and vinylidenecarbonate; vinyl thioesters such as vinyl methyl sulphide, vinyl n-butyl sulphides, 1-chloroethyl vinyl sulphides, 2-chloroethyl vinyl sulphide, vinyl dodecyl sulphide, vinyl phenyl sulphide, vinyl o-cresyl sulphide, vinyl 2,5-dimethyl-4-chlorophenyl sulphide, vinyl 8-chloronaphthyl sulphide, and vinyl 2-benzothiazylsulphide.

Also useful as comonomers are styrene and related monomers which copolymerise readily with the novel esters of this invention such as o-methylstyrene, p-methylstyrene, 3,4-dimethyl styrene, 2,4,6-trimethyl styrene, m-ethyl styrene, 2,5-diethyl styrene, p-butyl styrene, m-t-butyl styrene, p-benzyl styrene, o-methoxy styrene, p-methoxystyrene, 6-methoxy-3-methyl styrene, 2,6-dimethoxy styrene, and 2-methoxy-5-isopropyl styrene; derivatives of .alpha.-methyl styrene, such as: 4-chloro .alpha.-methyl styrene, 3,4-dimethyl .alpha.-methylstyrene, 3-bromo-2-methyl .alpha.-methylstyrene, and

2,5-dichloro-.alpha.-methylstyrene; chlorostyrene derivatives, such as m-chlorostyrene, 2,3-dichlorostyrene, 3,4-dichlorostyrene, trichlorostyrene, and pentachlorostyrene; bromo- and fluorostyrene derivatives, such as p-bromostyrene, m-fluorostyrene, m-trifluoromethyl styrene, 4-fluoro-3-trifluoromethyl styrene, and pentafluorostyrene; other styrene derivatives such as p-formylstyrene, methyl ester of p-vinyl benzoic acid, p-vinylbenzyl alcohol, 1,4-dimethyl-2-hydroxystyrene, 3,5-dibromo-4-hydroxystyrene, 2-nitro-4-isopropylstyrene, p-N,N-dimethyl amino styrene, N-(vinyl benzyl) pyrrolidine and sulphoamido styrene; vinyl derivatives of biphenyl, naphthalene and related aromatic compounds, such as 4-chloro-4'-vinyl biphenyl, o-isopropenyl biphenyl, p-vinyl diphenyl oxide, 4-chloro-1-vinyl naphthalene, 1-chloro-4-vinyl naphthalene and 1-vinyl acinaphthalene; vinylfuran, vinylbenzofuran, vinylimidazole and vinylpyridine, such as 2-vinyl dibenzofuran, 5-ethyl-2-vinyl-thiophene, 5-chloro-2-vinyl thiophene, 3,4,5-trichloro-2-vinyl thiophene and 2-vinyl dibenzothiophene.

Additional useful comonomers are ethylene and chloro-, fluoro- and cyano-derivatives of alkylene, such as ethylene, vinylchloride, vinylidene-chloride, vinylfluoride, vinylidene fluoride, acrylonitrile, methacrylonitrile, tetrafluoroethylene, trifluorochloroethylene, hexafluoropropylene; acrylate and methacrylate monomers, particularly those with 1 to 12 carbon atoms in the ester groups such as monofluoroethyl methacrylate, n-propyl methacrylate, 2-methyl cyclohexyl methacrylate, ethylene glycol mono-methacrylate, .beta.-bromoethyl methacrylate, .beta.-phenyl ether methacrylate, o-cresyl methacrylate, and .beta.-naphthyl methacrylate, methyl methacrylate, t-butyl methacrylate, n-butyl methacrylate, methylacrylate, ethylacrylate, propylacrylate, butylacrylate, 3-methyl-1-pentylacrylate, octylacrylate, tetradecylacrylate, s-butylacrylate, 2-ethylhexyl acrylate, 2-methoxyethyl acrylate, and phenyl acrylate, acrylic acid, methacrylic acid, .alpha.-halogen acrylates, such as methyl chloro acrylate, methyl bromo acrylate, ethyl chloro acrylate, s-butyl chloro acrylate, cyclohexyl chloro acrylate, phenyl chloro acrylate, cyclohexyl bromo acrylate, n-propyl chloro acrylate, isopropyl chloro acrylate, n-butylchloro acrylate, and methyl fluoro acrylate; dienes particularly 1,3-butadiene, isoprene, and chloroprene, 2-fluoro-butadiene, 1,1,3-trifluorobutadiene, 1,1,2,3-tetrafluoro butadiene, 1,1,2-trifluoro-3,4-dichlorobutadiene and tri- and pentafluoro butadiene and isoprene; nitrogen-vinyl monomers such as N-vinylimides, amides, and secondary cyclic amines, like vinyl succinimide, vinyl pyrrolidone, N-vinyl carbazole and the like.

Preferred co-monomers include alkyl(meth)acrylate units and/or (meth)acrylic acid and/or other vinylic compounds capable of forming polymerisable radicals (e.g. styrene,

n-propyl methacrylate, 2-methyl cyclohexyl methacrylate, ethylene glycol mono-methacrylate, tert-butylacrylate, iso-butyl methacrylate, iso-butyl acrylate, o-cresyl methacrylate, t-butyl methacrylate, n-butyl acrylate, n-butyl methacrylate, methylacrylate, methyl methacrylate, ethylacrylate, propylacrylate, iso-propyl methacrylate, 3-methyl-1-pentylacrylate, octylacrylate, tetradecylacrylate, s-butylacrylate, s-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-methoxyethyl acrylate, phenyl acrylate, acrylic acid, methacrylic acid, 1,3-butadiene, isoprene, vinyl pyrrolidone, acrylonitrile, methacrylonitrile, vinylimidazole and vinylpyridine, p-methylstyrene, 3,4-dimethyl styrene, m-ethyl styrene, p-butyl styrene, o-methoxy styrene, p-methoxystyrene, 2,6-dimethoxy styrene, isopropyl vinyl ether, isobutyl vinyl ether, vinyl 2-methoxy ethyl ether, n-hexyl vinyl ether, 2-ethylbutyl vinyl ether, n-octadecyl vinyl ether, .alpha.-methylvinyl ethyl ether, cyclohexanol vinyl ether, benzyl alcohol vinyl ether, vinyl phenyl ether, vinyl acetate, vinyl methoxyacetate, vinyl isobutyrate, vinyl oleate, vinyl benzoate, vinyloctylphthalate).

The co-polymer, may for example be a random copolymer, an alternating copolymer or a block copolymer. Preferably the co-polymer is a random copolymer.

The fluorinated polymer, used as an anti-cratering agent or levelling agent, may be present in a product (e.g. such as specified above) within a wide concentration range, of which the skilled professional will be able to determine a suitable concentration for a particular application.

Inter alia when the polymer is used in aqueous or organic solvent based lacquers, very good results have been achieved with a product comprising 0.1 - 10 wt.%, preferably 0.2 - 2.5 wt.%, more preferably 0.4 - 1.5 wt% of the fluorinated polymer. The amount of fluorinated units in the copolymer may be widely varied. In a preferred embodiment for a use according to the invention, the fluorinated polymer comprises 0.1 - 30 wt.% of the fluorinated units. When used as a levelling agent, very good results have been achieved with a composition (e.g. an aqueous or organic solvent based resin solution) containing a fluorinated polymer comprising 0.2 - 10 wt.% of the fluorinated units. Particularly good results have been achieved with a composition comprising a fluorinated polymer as a levelling agent wherein the fluorinated polymer comprises 0.5 - 4 wt.% of the fluorinated units.

In a particularly preferred use as an anti-cratering agent, the fluorinated polymer comprises 2 - 25 wt.% of the fluorinated units. Excellent results have inter alia been achieved when using a fluorinated polymer comprising 10 - 18 wt.% of the fluorinated units.

The present invention further relates to a novel polymer comprising at least one fluorinated monomeric unit represented by formula I, further comprising one or more alkyl(meth)acrylate units and/or (meth)acrylic acid and/or other moieties originating from vinylic compounds that can form radicals (e.g. styrene, n-propyl methacrylate, 2-methyl cyclohexyl methacrylate, ethylene glycol mono-methacrylate, tert-butylacrylate, iso-butyl methacrylate, iso-butyl acrylate, o-cresyl methacrylate, t-butyl methacrylate, n-butyl acrylate, n-butyl methacrylate, methylacrylate, methyl methacrylate, ethylacrylate, propylacrylate, iso-propyl methacrylate, 3-methyl-1-pentylacrylate, octylacrylate, tetradecylacrylate, s-butylacrylate, s-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-methoxyethyl acrylate, phenyl acrylate, acrylic acid, methacrylic acid 1,3-butadiene, isoprene, vinyl pyrrolidone, acrylonitrile, methacrylonitrile, vinylimidazole and vinylpyridine, p-methylstyrene, 3,4-dimethyl styrene, m-ethyl styrene, p-butyl styrene, o-methoxy styrene, p-methoxystyrene, 2,6-dimethoxy styrene, isopropyl vinyl ether, isobutyl vinyl ether, vinyl 2-methoxy ethyl ether, n-hexyl vinyl ether, 2-ethylbutyl vinyl ether, n-octadecyl vinyl ether, .alpha.-methylvinyl ethyl ether, cyclohexanol vinyl ether, benzyl alcohol vinyl ether, vinyl phenyl ether, vinyl acetate, vinyl methoxyacetate, vinyl isobutyrate, vinyl oleate, vinyl benzoate, vinyloctylphthalate). These polymers have been found to be very suitable as a wetting agent, an anti-cratering agent, a levelling agent, a binding agent, a dirt and stain repellent or a sizing agent. Particularly preferred alkyl(meth)acrylates in a novel polymer according to the invention or a polymer used in accordance with the invention include n-propyl(meth)acrylate, iso-propyl(meth)acrylate, n-butyl(meth)acrylate, sec-butyl(meth)acrylate, tert-butyl(meth)acrylate, iso-butyl(meth)acrylate, ethylhexyl(meth)acrylate and (meth)acrylic acid.

In a much preferred polymer according to the invention, R^1 , and optionally R^2 , represent linear fluoroalkyl moieties.

A polymer according to the invention or a polymer used in accordance to the invention preferably has a number average molecular weight in the range of 1,000 to 50,000 g/mol, more preferably in the range of 2,000 to 20,000 g/mol, e.g. in the range of 2,500 to 4,000 g/mol.

Very good results have also been achieved with a polymer having a polydispersity (M_w/M_n) in the range of 1 - 4, e.g. 1.1 - 2.

The polymer may be a living polymer, e.g. obtained by anionic polymerisation, atom transfer mechanism, nitroxide mediated techniques or other controlled polymerisation

techniques. A benefit of a living polymer is its tailor-made molecular architecture, combined with a narrower molecular weight distribution leading to smaller melting ranges and lower viscosities.

Very good results have also been obtained with a polymer in the form of a liquid or a solid (e.g. a powder), which is soluble in an organic solvent or in water, or made water-soluble after neutralization of acidic moieties. Such a system is particularly suitable for water-based systems.

Suitable neutralizing agents for neutralising acidic moieties are e.g. dimethylethanolamine, ammonia, other primary, secondary or tertiary amines or alkali hydroxides. An advantage of using a volatile amine neutralizing agent is that during the drying phase of a paint film, the amine neutralizing agent evaporates, leaving behind a more water resistant polymer.

In principle, a polymer comprising at least one fluorinated unit represented by formula I may be prepared in anyway, e.g. by a thermal radical, controlled radical, anionic or cationic polymerisation technique, of which the skilled professional will know how to employ them. The monomer compounds of the present invention may be prepared following procedures familiar to those skilled in the art.

Starting materials employed are generally commercially available and/or may be prepared readily according to methods familiar to those skilled in the art.

It is to be understood that the perfluoroalkyl group may, if desired, be a mixture of varying chain length since basic starting materials are often obtained by telomerization procedures yielding fluoroalkyl groups of varying length. U.S. Pat. No. 3,226,449 is illustrative of one method useful for the preparation of certain perfluoroalkyl iodides which may be employed as starting materials in making the monomers for preparing a polymer of the present invention.

The ester monomers of this invention can generally be prepared by well known esterification reactions between: cyclic anhydrides and perfluorinated alcohols, acids and perfluorinated alcohols or alkyl esters and perfluorinated alcohols, Of course, it is understood that the corresponding mercaptans and amines may be used in lieu of the alcohols. The esterifications may be carried out in the absence of a catalyst.

Typically, the fluorinated alcohol is mixed with an equimolecular amount of maleic anhydride, and heated to $> 40^{\circ}\text{C}$, at which temperature the exothermic ring opening of the cyclic anhydride starts to take place to form the monomaleate of the fluorinated

alcohol. This reaction can be carried out without addition of a solvent or catalyst, but optionally can take place in non-protic solvents like esters, aromatic hydrocarbons, ketons and the like at concentration of not less than 50%. As catalysts, metal salts and metal complexes can be added at < 1%, such as dibutyl tin dilaurate and tetraisopropyl titanate. The conversion can be determined by ¹H-NMR or by measurement of the acid value.

For the synthesis of a diester of maleic acid, the monoester is formed as above and the second ester is practically esterified at temperatures above 150 °C in the presence of a solvent that forms an azeotrope with the formed reaction water like xylene and a catalyst such as p-toluenesulphonic acid.

Other methods to obtain mono- and difluoroalkyl esters of maleic acid from fluorinated alcohols are transesterification reactions with maleic diesters of low boiling alcohols such as diethylmaleate and dibutylmaleate, by which the alkyl groups of the esters are exchanged by the fluoroalkylchains, in the presence of an organic titanate and optionally a solvent at elevated temperatures, under removal of the liberated alkyl alcohol.

When the corresponding amines, e.g. pentadecafluorooctyl amine, are used instead of the alcohols, maleimides are formed instead of the half esters of maleic acid, if the reaction is conducted with equimolar amounts of the maleic anhydride or maleic acid and the fluorinated amine.

Polymerisation of the obtained mono- or difluoroalkyl maleic derivatives may be carried out in bulk, solution, suspension, or emulsion.

As indicated above, the monomers suitable for preparing a polymer in accordance with this invention may be copolymerised with one or more other ethylenically unsaturated comonomers. A preferred polymerisation technique is thermal random solution polymerisation.

In thermal random solution polymerisation, the monomer or mix of monomers is/are added over a period of time to a suitable solvent such as aromatic and aliphatic hydrocarbons (e.g. xylene, toluene), ketones (e.g. acetone, butanone, methyl isobutyl ketone), esters (e.g. ethyl acetate, butyl acetate, methoxy propyl acetate), alcohols (e.g. s-butanol, iso-butanol, iso-propanol, (poly)ethylene glycol, (poly)propylene glycol), water, glacial acetic acid or mixtures thereof in a reaction vessel using initiators such as azobisisobutyronitrile or other azo initiators, or di-tert-butylperoxide or other peroxides and peroxyesters at concentrations of 0.1 to 5.0% at reaction temperatures of 40 to 160 °C, e.g. under nitrogen.

Valuable copolymers are obtained by polymerisation of the foregoing perfluorinated monomers with other polymerisable monomers having ethylene unsaturation, such as mentioned above

The invention further relates to compositions comprising a novel polymer according to the invention. A polymer according to the invention may for example very suitably be used in a composition like a coating, printing ink or plastic compound.

Such a product may for example further comprise one or more pigments, e.g. chosen from the group consisting of phthalocyanines, carbon black, titanium dioxide, ferrous oxides, aluminosilicates, quinacridones, anthraquinones, diketopyrrolo-pyrrole, benzimidazolones and isoindolinones, one or more extenders, e.g. calcium carbonate, barium sulphate, silicon dioxide, aluminium trihydroxide, organic fibres, glass and optionally one or more dispersants, e.g. polyurethane dispersants, polyester dispersants, polyacrylate dispersants, polyether derivatives, fatty acid derivatives, alkylsulphates.

A polymer according to the invention may very suitably be used in a dispersion, comprising 0 - 85 %, by weight, preferably 3 to 70%, of pigment and/or extender, 0.1 - 5% by weight, preferably 0.4 to 1.5% of a fluorinated polymer according to the invention, 10 - 95% by weight, preferably 25 to 40% of a resin, 0 - 90% by weight preferably 20 to 50% of water and/or non-aqueous liquid and 0 - 15% by weight preferably 1 to 5% of dispersant. Very good results have been achieved with a dispersant which mainly consists of these components.

The invention will now be illustrated by some examples.

EXPERIMENTAL

General procedure for fluorinated intermediates:

Intermediate A:

Under a nitrogen atmosphere, maleic anhydride (8.6 g, 1 equivalent) and Zonyl FSO-100 (MW ca. 725, 64 g, 1 equivalent) were placed in a reactor at room temperature and heated to 120 °C in one hour. No solvent or catalyst were added. After 3 h the intermediate A was obtained as a yellowish liquid.

In a similar way the following intermediates (B to F) were prepared:

Intermediate B: with 4 g of maleic anhydride and 18.1 g of Zonyl BA-L (MW ca. 443), yellow solid.

Intermediate C: with 16 g of maleic anhydride and 75.8 g of Fluowet EA800 (MW ca. 464), white solid.

Intermediate D: with 15.5 g of maleic anhydride and 150 g of Zonyl FSN-100 (MW ca. 950), waxy solid.

Intermediate E: with 2.84 g of citraconic anhydride and 11.35 g of Fluowet EA 612 (MW ca. 448), white solid.

Intermediate F: with 5.66 g of maleic anhydride and 27.45 g of Foralkyl EOH-6N-LW (MW ca. 475), white solid.

Intermediate G: Under a nitrogen atmosphere, maleic anhydride (5.66 g, 1 equivalent), xylene (60 g), Foralkyl EON-6N-LW (54.83 g, MW ca. 475, 2 equivalents) and toluene-4-sulphonic acid (0.5 g) are refluxed. The reaction water is distilled off under azeotropic conditions. The esterification is complete when the calculated amount of reaction water is separated. After the solvent removal, the intermediate G is obtained as a yellowish wax.

Legend to chemical compositions of trade mark fluoroalcohols:

Zonyl BA-L: mixture of linear fluoroalcohols $R_fCH_2CH_2OH$ with $R_f = C_4F_9 < 4\%$, C_6F_{13} 50 +/- 3%, C_8F_{17} 29 +/- 2%, $C_{10}F_{21}$ 11 +/- 2% and fluorinated compounds $C_{12}F_{25}$ less than 6%. The average MW of the mixture is 443 g/mol; the mixture is originating from DuPont

Zonyl FSO-100: mixture of ethoxylated linear fluoroalcohols $R_fCH_2CH_2O(CH_2CH_2O)_yH$ with $y = 0$ to 15, $R_f = C_4F_9 < 4\%$, C_6F_{13} 50 +/- 3%, C_8F_{17} 29 +/- 2%, $C_{10}F_{21}$ 11 +/- 2% and fluorinated compounds $C_{12}F_{25}$ less than 6%. The average MW of the mixture is 725 g/mol; the mixture is originating from DuPont

Zonyl FSN-100: mixture of ethoxylated linear fluoroalcohols $R_fCH_2CH_2O(CH_2CH_2O)_yH$ with $y = 0$ to 25, $R_f = C_6F_{13}$ 50 < 6%, C_8F_{17} 50 +/- 3%, $C_{10}F_{21}$ 29 +/- 2%, $C_{12}F_{25}$ 11 +/- 2% and $C_{14}H_{29} < 4\%$. The average MW of the mixture is 950 g/mol; the mixture is originating from DuPont.

Fluowet EA800: linear fluoroalcohol $C_8F_{17}CH_2CH_2OH > 98\%$ with MW of 464 g/mol; originating from Clariant.

Fluowet EA 612: mixture of linear fluoroalcohols $R_fCH_2CH_2OH$ with $R_f = C_6F_{13}$ 42 +/- 4%, C_8F_{17} 31 +/- 3%, $C_{10}F_{21}$ 14,5 +/- 2,5% and fluorinated compounds $C_{12}F_{25}$ less than 10% and the average MW of the mixture is 448 g/mol; the mixture is originating from Clariant.

Foralkyl EON-6N-LW: mixture of linear fluoroalcohols $R_fCH_2CH_2OH$ with $R_f = C_6F_{13}$, 45 +/- 10%, C_8F_{17} , 36 +/- 10%, $C_{10}F_{21}$, 12 +/- 5% and fluorinated compounds $C_{12}F_{25}$ less than 10% and the average MW of the mixture is 475 g/mol; the mixture is originating from Atofina.

Fluorad FC 10: mixture of linear fluoroalcohols: *N*-ethyl perfluorooctane sulphonamidoethyl alcohol 85 +/- 5%, *N*-ethyl perfluoro C_4 - C_7 -alkyl sulphonamidoethyl alcohols 15 +/- 5% and the average MW of the mixture is ca. 575 g/mol; the mixture is originating from 3M.

Levelling agent:

General procedure for synthesis of acrylic polymers:

Example 1:

Xylene (30 g) was placed in a three necked flask under a nitrogen atmosphere and heated to reflux (140 °C). The premix consisting of 76.18 g *n*-butylacrylate, 21.13 g of iso-butylmethacrylate, 0.73 g of intermediate A and 1.96 g of di-*tert*-butyl peroxide was added during 3 hours. After addition of the premix, the contents of the flask were stirred for another 4 hours at 140 °C. The solid content was corrected to 70% by addition of 6 g of xylene to obtain a yellowish clear liquid. The calculated molecular weight of the prepared polymer was approximately 3700 g/mol (M_n).

In the following examples a similar polymerisation procedure was followed

Example 2:

Levelling agent with the following premix:

<i>n</i> -butylmethacrylate	65.08 g
iso-butylacrylate	21.46 g
methacrylic acid	9.00 g
intermediate B	2.21 g
di- <i>tert</i> -butyl peroxide	2.25 g
60% in <i>s</i> -butanol, yellowish, slightly hazy liquid	

The mixture was polymerised as described in Example 1.

Example 3:

Levelling agent: with the following premix:

n-butylacrylate	85.40 g
ethylhexylacrylate	11.89 g
intermediate C	0.91 g
di-tert-butyl peroxide	1.80 g
50% in xylene/s-butanol (4:1), yellowish, slightly hazy liquid	

The mixture was polymerised as described in Example 1. The calculated molecular weight of the prepared polymer was approximately 4000 g/mol (Mn).

Example 4:

Anti-cratering agent with the following premix:

iso-butylmethacrylate	14.38 g
methacrylic acid	15.23 g
n-butylacrylate	51.90 g
intermediate A	16.54 g
t-butyl peroxy-2-ethylhexanoate	1.95 g
60% in s-butanol, clear slightly yellow liquid	

The mixture was polymerised as described in Example 1.

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Example 5:

Anti-cratering agent with the following premix:

iso-butylmethacrylate	14.38 g
methacrylic acid	15.23 g
n-butylacrylate	51.90 g
intermediate D	16.54 g
t-butyl peroxy-2-ethylhexanoate	1.95 g
75% in xylene, yellowish, slightly hazy liquid	

The mixture was polymerised as described in Example 1.

Example 6:

Anti-cratering agent with the following premix:

n-butylacrylate	65.71 g
iso-butylmethacrylate	18.16 g
intermediate E	14.19 g
di-tert-butyl peroxide	1.94 g
50% in xylene, yellowish, slightly hazy liquid	

The mixture was polymerised as described in Example 1.

Example 7:Anti-cratering agent: *in situ addition*, with the following premix:

n-butylacrylate	65.71 g
iso-butylmethacrylate	18.16 g
maleic anhydride	2.07 g
di-tert-butyl peroxide	1.94 g
60% in xylene	

Conditions were as in Example 1, but the fluorinated compound, Fluorad FC 10 (MW ca. 575) was added after polymerisation of the premix in an amount of 12.12 g to the reaction mixture at 100 °C and stirred for 6 hours, to obtain the final product as a yellowish liquid.

Example 8:

Anti-cratering agent with the following premix:

iso-butylmethacrylate	12.46 g
methacrylic acid	13.24 g
n-butylacrylate	42.35 g
intermediate F	30.00 g
t-butyl peroxy-2-ethylhexanoate	1.95 g
50% in sec-BuOH/IPA (3:2), yellowish slightly hazy liquid	

The mixture was polymerised as described in Example 1.

Example 9:

Polyethyleneglycol monomethylether Mw 350 (60.0 g) and intermediate F (19.6 g) were added to a three necked flask under a nitrogen atmosphere and heated to 120 °C.

The premix, consisting of 94.2 g of n-butylacrylate, 15.3 g of acrylic acid and 10.9 g of tert-butylperoxybenzoate, was added during 3 hours. After addition of the premix, the content of the flask was stirred for another 4 hours at 120 °C. The resulting polymer is a slightly hazy yellowish liquid.

The polymer was neutralised with 134.0 g of aqueous KOH solution (concentration 11%), resulting in a yellowish clear liquid with 45% of active substance.

APPLICATION TESTS

Example A1: Aqueous lacquer: acrylic emulsion

Joncryl 8051	90.74 g	
Aqueous Colour Paste with		
40% Heliogen Blue L 7072 D	0.91 g	
Water	8.15 g	
EFKA-2526	0.2 g	100 g
Example 2	1.0 g	
Dimethylaminoethanol	0.1 g	

The components were added in sequence, and stirred under a dispermat at 2000 rpm for 5 minutes. The samples were applied as a draw-down with a 75 μ bar coater on polyester foil. After air drying the levelling was checked visually and showed a significant better levelling than a sample being treated with a comparison lacquer composition that contained the same ingredients, with exception of the fluorinated polymer of Example 2 and the neutralising amine.

Example A2: Solvent-based lacquer: polyurethane

Macrynal SN 510	88.6 g	
Butylacetate	9.9 g	
EFKA-2018	1.5 g	100 g
Example 1	1.0 g	

The components were added in sequence, and stirred by hand until homogeneous. Then the hardener (35 g of Desmodur N75 on above formulation) was added and stirred by hand until homogeneous. The samples were applied as a draw-down with a 75 μ bar coater on polyester foil. The levelling was checked visually after 24 h of air-drying and showed a significant better levelling than a sample being treated with a comparison lacquer composition that contained the same ingredients, with exception of the fluorinated polymer of Example 1.

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Example A3: Solvent-based lacquer: polyurethane

Macrynal SN 510	88.6 g	
BuOAc	9.9 g	
EFKA-2018	1.5 g	100 g
Example 8	0.2 g	

The components were added in sequence, and stirred under a dispermat at 4000 rpm for 15 minutes. Then the hardener (35 g of Desmodur N75 on above formulation) was added and stirred by hand until homogeneous. The samples were applied as a draw-down with a 75 μ bar coater on polyester foil. The levelling was checked visually after 24 h of air-drying. After air drying the levelling was checked visually and showed significantly better levelling than a sample being treated with a comparison lacquer composition that contained the same ingredients, with exception of the fluorinated polymer of Example 8.

Example A4: Solvent-based lacquer: stoving alkyd melamine

Vialkyd AC 451	54.0 g	
Solvesso 100	16,7 g	
Maprenal F 650	29.0 g	
EFKA-3033	0.30 g	100 g
Example 7	0.20 g	

The components without Example 7 were added in sequence, and stirred by hand until homogeneous. Two samples were applied as a draw-down with a 75 μ bar coater on polyester foil. After 10 minutes of flash-off time, the samples were cured by 30 minutes baking at 135 °C. A second layer, one containing Example 7 and one without, was applied with the same film thickness over the first layer and cured under the same conditions including flash-off time. The levelling and wetting were checked visually and compared with a comparison lacquer composition that contained the same ingredients, with exception of the fluorinated polymer of Example 7. The lacquer comprising the fluorinated polymer of Example 7 showed a much better levelling and wetting.

Example A5: Solvent based lacquer: epoxyEpoxy formulation:

Epikote 1001	80.5 g	
Xylene	9.2 g	
Isobutanol	3.1 g	
Butylglycol	6.2 g	
EFKA-2021	1.0 g	100 g
Example 6	0.2 g	

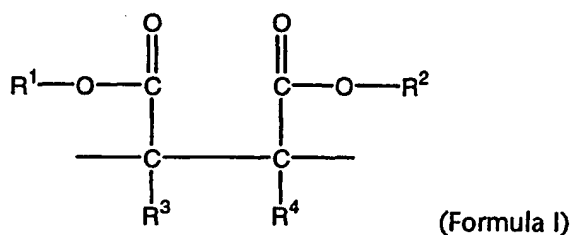
Hardener formulation:

Eurodur 115/70X	63.1 g	
Xylene	6.9 g	
Isobutanol	30.0 g	100 g

The components were added in sequence, and stirred by hand until homogeneous. Then 68.7 g of the hardener (see formulation above) was added on above epoxy formulation and stirred by hand until homogeneous. The samples were applied as a draw-down with a 75 μ bar coater on polyester foil. The levelling was checked visually after 24 h of air-drying. The sample showed better levelling than the comparison sample without addition of the polymer of Example 6.

Claims

1. Use of a polymer as a levelling agent or anti-cratering agent, said polymer comprising at least one fluorinated unit represented by formula I,



wherein R^1 is a moiety selected from the group consisting of $C_nF_{2n+1}-(CH_2)_m-$, $AC_nF_{2n}-(CH_2)_m-$, $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p$, $C_nF_{2n+1}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p-X$ or $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p-X-$;

wherein A is selected from the group consisting of H, Cl, Br, I, C_{1-12} alkyls and OC_{1-12} alkyls,

wherein $4 \leq n \leq 20$, $0 \leq m \leq 4$ and $0 \leq p \leq 20$,

wherein X is a spacer moiety selected from the group consisting of esters, amides, sulphoamides, mercapto groups, polyurethane groups and alkyl groups,

wherein R^2 is selected from the group consisting of H, metal moieties, (alkyl)ammonium moieties, alkyl groups, $C_nF_{2n+1}-(CH_2)_m-$, $AC_nF_{2n}-(CH_2)_m-$, $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p$, $C_nF_{2n+1}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-X-$, $AC_nF_{2n}-(CH_2)_m-(OCH_2CHR^5)_p-X$ and $C_nF_{2n+1}-(CH_2)_m-(OCH_2CHR^5)_p-X-$;

wherein A is selected from the group consisting of H, Cl, Br, I, C_{1-12} alkyls and OC_{1-12} alkyls,

wherein $4 \leq n \leq 20$, $0 \leq m \leq 4$ and $0 \leq p \leq 20$,

wherein X is a spacer moiety selected from the group consisting of esters, amides, sulphoamides, mercapto groups, polyurethane groups and alkyl groups,

wherein R^3 and R^4 are independently selected from the group consisting of H, alkyl-groups and phenyl-groups

and wherein R^5 is selected from the group consisting of H and methyl groups.

2. Use according to claim 1, wherein said polymer comprises a fluorinated unit content of 0.1 - 30 wt.%.
3. Use according to claim 1 or 2, wherein at least 50%, preferably 90 - 100% of the fluorinated units are mono-esters
4. Use according to any of the preceding claims, wherein at least 50%, preferably 70 - 100% of the fluorinated units of the polymer are represented by formula I wherein n is 4 - 14
5. Use according to any of the preceding claims, wherein m is 2.
6. Use according to any of the preceding claims, wherein p is 0 or 6 - 8.
7. Use according to any of the preceding claims wherein R¹ and/or R² represents a linear fluoroalkyl moiety.
8. Polymer comprising at least one fluorinated monomeric unit represented by formula I, said polymer further comprising at least one alkyl(meth)acrylate unit, styrene or vinylacetate.
9. Polymer according to claim 8, wherein one or more alkyl(meth)acrylates are selected from the group consisting of n-propyl(meth)acrylate, iso-propyl(meth)acrylate, n-butyl(meth)acrylate, sec-butyl(meth)acrylate tert-butyl(meth)acrylate, iso-butyl(meth)acrylate, ethylhexyl(meth)acrylate and (meth)acrylic acid.
10. Polymer according to claim 8 and 9, comprising a fluorinated unit content of 0.1 - 30 wt.%.
11. Polymer according to any of the claims 8 - 10, wherein at least 50%, preferably 90 - 100 % of the fluorinated monomeric units are mono-esters.
12. Polymer according to any of the claims 8 - 11, wherein at least 50%, preferably 70 - 100 % of the fluorinated units of the polymer are represented by formula I and wherein n is 6 - 8 .

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13. Polymer according to any of the claims 8 - 12, wherein R¹ represents a linear fluoroalkyl moiety.
14. Polymer according to any of the claims 8 - 13, which has the form of a random copolymer, a block copolymer, preferably a random copolymer.
15. Polymer according to any of the claims 8 - 14, which has a number average molecular weight in the range of 1,000 to 50,000 g/mol, preferably in the range of 2,000 to 20,000 g/mol.
16. Polymer according to any of the claims 8 - 15, with a polydispersity (M_w/M_n) in the range of 1 - 4.
17. Polymer according to any of the claims 8 - 16, characterized in that it is a living polymer
18. Polymer according to any of the claims 8 - 17, in the form of a liquid, solid (e.g. a powder), which is soluble in an organic solvent or directly in water, or alternatively soluble in water after neutralization of acidic moieties.
19. Coating, printing ink or plastic compound comprising a polymer according to any of the claims 8 - 18, a pigment and optionally a dispersant.
20. Coating, printing ink or plastic compound according to claim 19, comprising an extender.
21. A dispersion, comprising 0 - 85% by weight of pigment and/or extender, 0.1 - 5 % by weight of a polymer according to any of the claims 8 - 18, 10 - 95 % by weight of a resin, 0 - 90% by weight of water and/or non-aqueous liquid and 0 - 15% by weight of dispersant.
22. An article treated with a polymer according to claim 8 - 18 or with a coating, plastic compound or printing ink according to claim 19 or 20 or a dispersion according to claim 21.

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23. Use of a polymer according to claim 8 - 18 as a levelling agent, a wetting agent, an anti-cratering agent, a binding agent, a soil-repellent or a sizing agent.

24. Use of a moiety comprising a fluorinated unit represented by formula I in the manufacture of a polymeric levelling agent or polymeric anti-cratering agent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/11237

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D7/06 C09D11/02 C08F222/18 C08F222/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 770 656 A (PECHHOLD ENGELBERT) 23 June 1998 (1998-06-23) cited in the application column 2, line 5-50 column 3, line 15-45 column 5, line 63-67 ---	8, 11-14, 19, 22, 23
X	DE 19 18 079 A (J.R. GEIGY AG) 16 October 1969 (1969-10-16) page 6, line 25-27 page 7, line 25 page 8, line 5 page 8, line 30-33 page 10, line 7-9 & US 4 075 237 A 21 February 1978 (1978-02-21) cited in the application ---	8, 9, 12-14, 19, 22, 23
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 776 914 A (DAIKIN IND LTD) 4 June 1997 (1997-06-04) claims 1,2,9 ----	8-10, 12-15
A	DATABASE WPI Section Ch, Week 200029 Derwent Publications Ltd., London, GB; Class A14, AN 2000-332358 XP002193580 & JP 2000 102727 A (DAINIPPON INK & CHEM INC), 11 April 2000 (2000-04-11) abstract ----	1,19, 21-23
A	US 5 030 684 A (RAUCH-PUNTIGAM HARALD ET AL) 9 July 1991 (1991-07-09) abstract; claim 1 ----	1,19, 21-23
A	EP 0 537 669 A (NOF CORP) 21 April 1993 (1993-04-21) page 16, line 9-35; claims 7-10 -----	1,19, 21-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/11237

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5770656	A	23-06-1998	AU 726303 B2	02-11-2000
			AU 6975396 A	09-04-1997
			DE 69618970 D1	14-03-2002
			DE 69618970 T2	29-08-2002
			EP 0851948 A1	08-07-1998
			JP 11514398 T	07-12-1999
			WO 9711218 A1	27-03-1997
DE 1918079	A	16-10-1969	US 4075237 A	21-02-1978
			CA 932498 A2	21-08-1973
			CH 495386 A	31-08-1970
			DE 1918079 A1	16-10-1969
			DE 1966209 A1	02-03-1972
			FR 2005992 A5	19-12-1969
			GB 1266408 A	08-03-1972
			NL 6905476 A	14-10-1969
			US 3884879 A	20-05-1975
			US 3763116 A	02-10-1973
			US 3794623 A	26-02-1974
EP 0776914	A	04-06-1997	JP 3235354 B2	04-12-2001
			JP 8003113 A	09-01-1996
			AT 203757 T	15-08-2001
			DE 69522003 D1	06-09-2001
			DE 69522003 T2	21-03-2002
			EP 0776914 A1	04-06-1997
			US 5830963 A	03-11-1998
			CA 2197430 A1	22-02-1996
			WO 9605237 A1	22-02-1996
JP 2000102727	A	11-04-2000	NONE	
US 5030684	A	09-07-1991	AT 390444 B	10-05-1990
			AT 238988 A	15-10-1989
			CA 1334040 A1	17-01-1995
			DE 58907568 D1	01-06-1994
			EP 0362643 A2	11-04-1990
			JP 2163176 A	22-06-1990
EP 0537669	A	21-04-1993	JP 5131130 A	28-05-1993
			JP 6016780 A	25-01-1994
			JP 6032842 A	08-02-1994
			JP 6056962 A	01-03-1994
			JP 6065261 A	08-03-1994
			CA 2080499 A1	15-04-1993
			EP 0537669 A1	21-04-1993
			JP 3269135 B2	25-03-2002
			JP 5222113 A	31-08-1993
			US 5414065 A	09-05-1995
			US 5324803 A	28-06-1994
			JP 5311149 A	22-11-1993
			JP 5339538 A	21-12-1993
			KR 9608481 B1	26-06-1996

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